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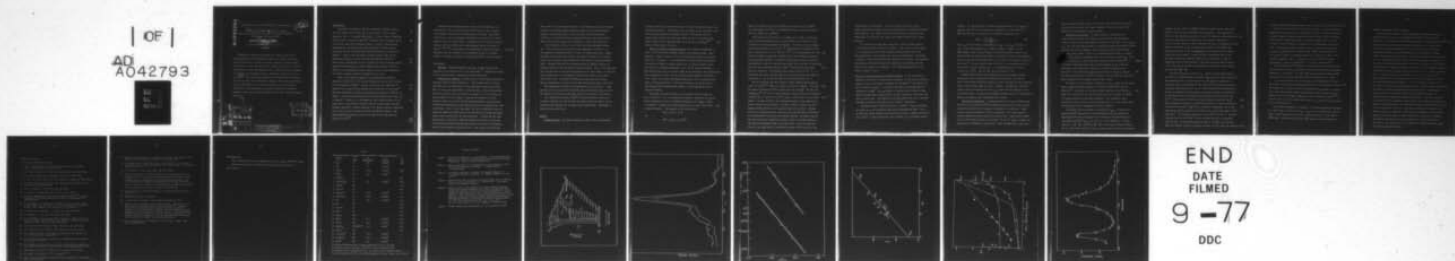
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MEDIUM EFFECTS ON TRANS-CR(NH₃)₂(NCS)₄(-) PHOSPHORESCENCE, (U)
JUN 77 A R GUTIERREZ, A W ADAMSON

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Medium Effects on Trans-Cr(NH₃)₂(NCS)₄⁺ Phosphorescence,

by Adolfo R. Gutiérrez and Arthur W. Adamson

Department of Chemistry, University of Southern California,
Los Angeles, California 90007

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Abstract

Lifetimes for doublet state emission of reineckate ion, trans-Cr(NH₃)₂(NCS)₄⁺, in room temperature solution are reported for twenty solvent media and as a function of solvent composition in water-acetonitrile mixtures. These vary from 6 nsec in water to 204 nsec in sulfolane (and 460 nsec for the solid potassium salt). Apparent activation energies for emission were determined in twelve systems and range from 10 to 18 kcal/mole⁻¹. Both the emission spectrum and the doublet state absorption spectrum are given for acetonitrile as solvent. The excited state kinetic scheme is discussed in terms of these and other data, and it appears likely that at room temperature the emission lifetimes are determined primarily by the rate at which the doublet excited state undergoes chemical reaction.

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Introduction

The present investigation comprises essentially a kinetic study of the first doublet thexi¹ state, D_1^0 , of a particular Cr(III) complex, (1)

Reineckate ion, R^- , or trans- $Cr(NH_3)_2(NCS)_4^-$. Figure 1 shows a simplified excited scheme for Cr(III) complexes;² excitation in the wavelength region (2)

of the first ligand field absorption band, L_1 , leads to substitutional photochemistry, the quantum yield characterization of which has been extensively studied both empirically and theoretically for a variety of species.² There is also intersystem crossing leading to D_1^0 , and low temperature emission from this state has been known for some time.³ (3)

More recently, Kane-Maguire and C.H. Langford⁴ were able to detect and give (4)
spectral characterization to doublet emission from a number of Cr(III) amines in room temperature, fluid solution, as well as some temperature and solvent dependence results (although not for R^- ion).

Turning to the present compound, the low temperature absorption spectrum of the D_1^0 state of R^- has been reported as well as some lifetimes in low temperature solvents.⁵ Further, the excited state absorption is (5)

found to occur within short picoseconds after excitation in the L_1 band.⁶ (6)

Thus some intersystem crossing occurs promptly and perhaps, as indicated in Figure 1, before thermal equilibration to the first quartet thexi state, Q_1^0 , is complete.⁷ Finally, in a low temperature (but fluid) solution, it was (7)

found that the photochemistry (which is release of thiocyanate) was only partially quenched on complete quenching of the doublet emission, indicating that a major fraction of reaction occurred from Q_1^0 and, moreover, that thermal Q_1^0 - D_1^0 interconversion could not be rapid on the time scale for reaction from Q_1^0 .^{8,9} (8,9)

(10)

Photochemical and emission yields, while of great importance, are controlled by ratios of excited state rate processes; to get at actual rate constants, some form of rate measurement is required. The present study centers on the one presently available kinetic quantity for Cr(III) complexes, that of the D_1^0 lifetime. Reineckate ion was chosen for several reasons. Both its thermal and its photochemistry have been studied in detail^{2,7,11,12,13}; its emission in room temperature solution was easily measurable with our equipment, as was absorption by D_1^0 ; it is readily soluble in a variety of solvents so that medium effects could be explored. (11,12,13)

Experimental.

Materials. Ammonium Reineckate (Matheson, Coleman, and Bell) was converted to the potassium salt in the usual manner.¹¹ Solvents were either of CP or spectral grade. Cryptate was obtained from Merck.

Procedures and equipment. Excitation was at 530 nm using an amplified, frequency doubled Nd laser (Korad Co.) . This yielded pulses of 20 nsec half-width time, as determined by a fast photodiode detector (Korad model KD1); in some cases, gating down to 3 nsec was done. Pulses were generally in the 50 to 200 mJ range, but could be increased to 1.5 J if desired; the beam was about 0.9 cm in diameter. Emission was monitored at 750 nm, isolated by means of an Oriel 7240 grating monochromator, and detected by an RCA 7265 photomultiplier whose signal was fed into a Tektronix model 7844 oscilloscope. This is a dual beam model, with two 7A19 amplifiers and two time bases (7B92A and 7B50A) and both the photodiode and the photomultiplier outputs could be observed on the same photograph. A Hanovia 900 watt high pressure Xe arc lamp and a 5 stage RCA 931A photomultiplier tube was used as the monitoring beam and the detection system respectively in determining excited state absorption spectra and decay. Both emission and monitoring

were at 90° to the laser pulse direction. Some emission spectra were obtained by means of a Princeton Applied Research Corporation Optical Multichannel Analyzer system consisting of a Jarrel Ash model 82-922 polychrometer, attached to an Intensified Silicon Intensified Target vidicon (model 12051) whose various channel signals were analyzed by a model 1205A OMA console.

The irradiation cell was a 1x1 cm four clear sided spectrofluorimeter cell. Cell and solution were either at room temperature, $23-25^\circ\text{C}$, or, in the temperature dependence studies, at that of a thermostatted bath. Samples generally were not deaerated; however, the emission lifetimes in air equilibrated and in nitrogen purged acetonitrile were identical within experimental error. Extensive drying of the acetonitrile gave no apparent variation in lifetime relative to that obtained in untreated solvent. Also, it was determined that lifetimes did not vary with the intensity of the laser pulse. On transcription to graph paper, the photographs of oscilloscope traces all gave first order decay rates: the reported lifetimes were calculated from a least squares fitting whose correlation coefficient was generally greater than 0.99.

Some experiments were made with perdeuterated KR in acetonitrile. A D_2O solution of KR was made alkaline with KOH, then acidified with D_2SO_4 to pH 2-3. The complex was precipitated with KNO_3 , dried, and dissolved in acetonitrile.

For experiments done with $\text{Cr}(\text{CN})_6^{3-}$ in acetonitrile-water mixtures the tetrabutyl ammonium salt was used when the amount of water was 20% or less by volume and the potassium salt at higher water concentrations. Wavelength of excitation was again 530 nm.

Results.

Emission spectra. The emission spectrum at 24°C for KR in acetonitrile

is shown in Figure 2, as obtained by means of the vidicon detector and optical multichannel analyzer. The principal peak, at 753nm, is that monitored in all of the lifetime studies, and reported earlier.⁴ Deuteration, while not significantly affecting the main peak, shifts certain of the shorter wavelength satellite ones, suggesting that, as in the case of $\text{Cr}(\text{NH}_3)_6^{3+}$,¹⁴ (14) ammonia vibration modes are active.

Effect of solvent on emission lifetime. The results are summarized in Table 1, with the systems arranged in order of increasing lifetime. Where indicated, cryptate in about 2 to 1 ratio by weight was added to solubilize the K^+ ion. Lifetimes, τ , were reproducible to about 10% both with respect to successive flashes of a given solution and, as tested in several cases, with respect to completely independent runs. For the shorter lifetimes, a 3ns flash was used, and in the case of H_2O , values obtained at lower temperatures were extrapolated to 23°C; even so, the 6ns lifetime quoted is uncertain to ± 1 ns. Again, in the case of solvents melting above 23°C, the reported lifetimes are extrapolated ones. In the case of system 2, the pH was made 2.0 with 2N D_2SO_4 before dissolving the complex, to avoid deuteration of the coordinated ammonia.

The apparent activation energy, E^* , was obtained from the slope of a plot of $\ln(1/\tau)$ vs. $1/T$. As illustrated in Figure 3, such plots were linear within experimental error; the probable uncertainty in E^* values is about ± 1 kcal/mole. The data obey a Barclay-Butler type of plot¹⁵ fairly well, (15) as shown in Figure 4. The equation of the line drawn is:

$$\ln A = 15.75 + 1.75 E^*$$

or

$$\Delta S^{\ddagger} = -28.18 + 3.48 \Delta H^{\ddagger}$$

where A is defined by $1/\tau = A \exp(-E^*/RT)$ and is given in sec^{-1} , $E^* = \Delta H^{\ddagger}$ is in kcal/mole, and ΔS^{\ddagger} is in cal/[(°K)(mole)] and is defined by $\ln(1/\tau) = 10^{13} \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT)$.

The lifetimes may be written in a formal way as $\tau = 1/(k_r + k)$ where k_r is the radiative probability and k is the collective rate constant for all non-radiative processes whereby D_1^0 disappears. The value of k_r is estimated from absorption spectra to be 35 sec^{-1} ; alternatively the lifetime at 77°K gives a maximum value of $3.2 \times 10^3 \text{ sec}^{-1}$.^{3,16} It is conventional (and, from (16) present knowledge, reasonable) to assume that k_r is not highly environment (or temperature) dependent. The theory of spontaneous emission invokes the wave-mechanical, that is, electron, n-pole field of the molecule as interacting with the initial and final vibronic states,¹⁷ and thus deals with intra- (17) molecular parameters. Our lifetimes give k values around 10^7 sec^{-1} , or much larger than either estimate above of k_r , and we conclude that under our conditions, $k \gg k_r$ so that our study is one of medium effects on k .

We have suggested that good ligand to solvent hydrogen bonding ability leads to a large k .¹⁸ Water as a ligand is better than ammonia. Thus while (18) the emission lifetimes at 77°K are about equal for $\text{Cr}(\text{NH}_3)_6^{3+}$ (56 μsec) and $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ (70 μsec), at room temperature aqueous solution the respective lifetimes are 1.8 μsec and $<5 \text{ nsec}$ ¹⁹ so that k is much larger for the latter (19) complex. The data of Table 1 give qualitative support to the importance of solvent hydrogen bonding ability; τ is small in water, alcohols, and other hydrogen bonding solvents, and relatively large for the others. Tertiary butanol is an exception which we excuse on steric grounds since the bulkiness of the hydrocarbon portion may limit hydrogen bonding. The general idea is that good vibrational communication between complex and solvent enhances k . The efficient quenching by THF, on the other hand, brings into focus the effect of the oxygen which is particularly exposed in this case due to the

cyclic nature of the molecule. It is not a matter of general solvent-complex interaction, however, since the lifetimes do not correlate particularly with solubility. For example, KR is much more soluble in acetonitrile and nitromethane than in water, but shows a much longer lifetime in the former solvents.

It is difficult to find other correlations. None is evident between τ and solvent viscosity (column 5 of Table 1). Also, there is little change in τ on passing from solid (clear glassy) sulfolane solution just below room temperature to fluid solution just above room temperature. The longest τ observed is that for solid KR powder suspended in chloroform. The absorption and emission are probably centered far enough from the interface that the nature of the latter is not important. The crystal thus appears to be the poorest "solvent" of all.

Effect of solvent composition on emission lifetime. It was of interest to examine the variation of τ with solvent composition for the water-acetonitrile system in view of the studies of Langford and co-workers.¹³ The results, for 24°C, are shown in Figure 5. Included in the figure are analogous data we obtained for $\text{Cr}(\text{CN})_6^{3-}$, the wavelengths of excitation and of emission being 530 nm (a strong pulse compensating for the small extinction coefficient) and 810 nm, respectively. The lifetimes in nitrogen purged water and in similarly deaerated acetonitrile were 410 nsec and 2.58 msec, respectively.

The behavior may be treated as follows. We write $k = k_i + k_s$ (neglecting k_r), where k_i is the contribution from purely intramolecular paths, and k_s is that from complex-solvent interaction sensitive paths. Judging from system 22 of Table 1, k_i may be relatively small compared to k_s in hydrogen bonding

solvents. In a mixed solvent, the formal treatment gives $k = k_i + k_1 g_1(N_1) + k_2 g_2(N_2)$, where the g 's are functions of composition. If the function is just mole fraction, N , one obtains for the water-acetonitrile case

$$\frac{\tau_{AN}}{\tau} = 1 + \frac{k_w - k_{AN}}{k_i + k_{AN}} N_w \quad (2)$$

where τ_{AN} is the lifetime in acetonitrile, $1/\tau_{AN} = k_i + k_{AN}$. The plot of τ_{AN}/τ is not linear against N_w , as shown in Figure 5. However, it is approximately linear if N_w is taken to be the mole fraction of water in the solvation shell as given by n/n_0 where n is the moles of water in the solvation shell in the mixed solvent system and n_0 is the moles in the solvation shell for pure water.¹³ One may, alternatively, treat water as a quenching species in Stern-Volmer kinetics, writing $\tau_{AN}/\tau = 1 + K_{SV} a_w^m$ where a_w is the water activity ($a_w = P/P^0$). The data fit with the exponent $m = 10$.

Neither approach above can be pushed very far as to physical meaning. From the n/n_0 data, acetonitrile preferentially solvates R^- ion, and not until a fairly large system mole fraction of water is present is there sufficient water in the solvation shell to affect τ strongly. Alternatively, one would conclude that the transition state for k_w contains ten water molecules in the R^- solvation shell. The behavior of $Cr(CN)_6^{3-}$ resembles that of R^- ion (Figure 5); however, no solvation shell compositions are available.

Excited State Absorption. A transient absorption occurs, following flash excitation of a solution of KR.¹⁹ This absorption decays with the same lifetime as does the emission and is therefore attributable to the D_1^0 state. Figure 6 shows a spectrum obtained at 20°C in acetonitrile. It is very similar to the low temperature spectra reported by Ohno and Kato.⁵ These authors suggest that in -61°C acetone solution new transients "R" and "X" appear, although they observed no "X" transient in acetonitrile. Their equipment may not have been

able to observe lifetimes shorter than 20 μ sec, while the Figure 6 data were collected in the 20 nsec time region. However, a search for longer lived transients in acetonitrile was not successful.

Excited State Mechanisms. The three potential contributions to k (other than k_r) are those from chemical reaction of D_1^0 , back intersystem crossing of D_1^0 to Q_1^0 , and non-radiative relaxation of D_1^0 to Q_1^0 : $k = k_{cr} + k_{bisc} + k_{nr}$. There has been much interest in assessing the relative importance of these processes for Cr(III) complexes, and we examine here what may be inferred from the present results. First, the correlation shown in Figure 4 suggests that no basic change in mechanism occurs over the range of our systems. This type of correlation is often found for a series of related reactions²⁰, a (20,21) qualitative explanation being that the bond weakening in the transition state gives closer vibrational spacings and increased transition state entropy.²² If the mechanism varies along the series of reactions, however, (22) no correlation between $\ln A$ and E^* is expected. We thus infer that one of the above components of k is dominant over our whole series.

Our results could be assigned to variations in k_{nr} . Because of the fairly high activation energies observed, the "strong coupling" model would be indicated.²³ And because of the strong solvent dependence, the vibrational (23) ladder to be ascended in the activation process would be expanded in concept to include complex-solvation shell vibrations. This explanation may be specious; it does not seem to carry any predictions or to relate other aspects of the general body of information on Cr(III) complexes.

Our results could be assigned to variations in k_{bisc} . In the case of aqueous $Cr(en)_3^{3+}$ that portion of the photochemistry that was quenched on quenching D_1^0 emission was suggested to be derived from Q_1^0 produced by back intersystem crossing¹⁰; k_{bisc} would then be of major importance. On this basis, $E^* \approx (Q_1^0 - D_1^0) + \delta E^*$ where $(Q_1^0 - D_1^0)$ is the energy difference between the two thexi states, and δE^* is the activation energy for forward intersystem

crossing, if any. While the $(Q_1^0 - D_1^0)$ difference could be in our range of E^* values it does not seem sufficiently solvent sensitive. There are solvent effects on the absorption spectrum of R^- ion,²⁴ but insofar as band maxima can (24) be used to judge the state separations, the frequency shifts over a range of solvents similar to that studied here are only a few hundred cm^{-1} and, moreover, the shifts in the L_1 maxima parallel those in the doublet band absorption features, so that the separation of band maxima does not change significantly with solvent. Further, we see no appreciable shift in the D_1^0 transient absorption spectrum between water, acetonitrile, or the low temperature matrix of Ohno and Kato.⁵ One could assign our solvent effects to δE^* , but there is no basis for expecting that δE^* should be more solvent sensitive than $(Q_1^0 - D_1^0)$.

The third possibility is that $k \approx k_{cr}$. While it is generally accepted that much of the photochemistry of Cr(III) complexes occurs from the Q_1^0 state² (and perhaps most of it, in the case of the less symmetric complexes), in some cases D_1^0 has been implicated. Chen and Porter⁸ found that the quantum yield, ϕ , for photoreaction of R^- ion in a -65°C methanol-water-ethylene glycol solvent was 0.010 and was 50% quenched on complete quenching of D_1^0 emission. It was proposed that the quenchable yield represented direct reaction from D_1^0 .²⁵ We now interpret E^* as the activation energy for reaction from D_1^0 . (25)

Thermal activation energies for substitution reactions of Cr(III) amines are in the 20-25 kcal mole^{-1} range,²⁶ and it seems not unreasonable that the D_1^0 (26) state should require activation for reaction, but in the lesser range of 10-18 kcal mole^{-1} . The entropy of aquation is 3 $\text{cal K}^{-1}\text{mole}^{-1}$ for R^- ; ²⁷ we would calculate about 14 $\text{cal K}^{-1}\text{mole}^{-1}$ for the reaction from D_1^0 , an acceptable type of value. It also seems significant that our k values are relatively small for solvents in which the thermal solvolysis is also small, and relatively large

for those in which the thermal solvation rate is large (water, ethanol, methanol¹²).

Thus this third mechanistic scenario is as follows. In room temperature, fluid solution, fraction f of the Franck-Condon quartet excited state produced by light absorption undergoes prompt intersystem crossing to D_1^0 , and fraction $(1-f)$ thermally equilibrates to Q_1^0 ; f is relatively small for R^- . Most of ϕ is due to reaction from Q_1^0 , in competition with radiationless deactivation to Q_0^0 . D_1^0 disappears mainly by chemical reaction (release of thiocyanate), and while k_{cr} determines the lifetime of D_1^0 , $\phi(D_1^0)$, the contribution to ϕ of reaction from D_1^0 , is determined mainly by f . There is, in fact, little correlation between ϕ and τ . We find ϕ to be 0.29 in water¹¹, 0.20 in nitromethane²⁷, and 0.23 in methanol²⁷; it is 0.16 in acetonitrile¹³.

At low temperatures^{7,8} f probably increases because of increased solvent cage restriction, but k_{cr} has decreased to the point that the less temperature dependent k_{nr} is dominant. The yield $\phi(D_1^0)$ is therefore small although $\phi(Q_1^0)$ also decreases so that the quenchable fraction of reaction may be large.

In the mixed solvent case, we require k_{cr} to be comparable to the rate of solvent-solvation shell interchange, which seems to be reasonable (note Ref. 28). The finding that τ and hence (in this interpretation) k_{cr} depends in a simple way on the solvation shell rather than the global solvent composition rather suggests that no thermodynamic sampling of solvent activities occurs.^{13,29} On the other hand, we see no multiple decay times, so k_{cr} must not be fast compared to the interchange rate.

Some further experiments are suggested. The extreme temperature dependence of τ should show a transition from k_{cr} to k_{nr} to k_r as dominant path; Ohno and Kato's results⁵ suggest that the first transition may occur in the -20°C to -80°C range. Both the yield of D_1^0 and $\phi(D_1^0)$ should similarly be studied to

establish the nature of the correlation.

That part of the scenario dealing with prompt intersystem crossing has been questioned in the cases of $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{en})_3^{3+}$ because of a non-dependence of E^* (for ϕ_p , the emission yield from D_1^0) on excitation wavelength.³⁰ (30)

It was assumed that the prompt intersystem crossing yield, f , determined E^* for ϕ_p , the temperature dependence of f arising from that of the solvent restricted relaxation of Q_{FC} to Q_1^0 where Q_{FC} is the collection of Franck-Condon states produced on excitation. It was therefore supposed that excitation at the long wavelength tail of the L_1 band should produce a near- Q_1^0 state, for which the temperature dependence of intersystem crossing would be different. That some prompt intersystem crossing occurs with R^- ion is established, however.⁶

In addition, the above reasoning seems to have two openings. First, ϕ_p depends both on f and on k_r/k , but it is possible (as we have) to assign E^* to k (k_{cr}) rather than to f (we would expect the temperature dependence of f to be more like that of liquid viscosities). It is not necessary, then, for E^* to be sensitive to excitation wavelength even if f is. There is another uncertainty. Excitation at various wavelengths leads to distributions of Franck-Condon states that do not necessarily involve the same vibrational ladder of excitations that is traversed on thermal equilibration. The first situation is governed by overlap integrals, and the other by how energy best flows from solute to solvent; the first one determines the shape of the absorption band, but it is the second that controls f . The point is illustrated in Figure 1, in which two ladders are indicated. There can be a multiplicity of such ladders because of the large number of normal coordinates, especially if in thermal equilibration one adds solute-solvent vibrations to the molecular ones of the complex. This aspect makes it very difficult to affirm just how f should vary with excitation wavelength.

References and Notes

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Acknowledgement

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Table I

Solvent Dependence of Doublet Emission Lifetime of $\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_4^-$ ^a				
Solvent	τ^b nsec	E^* kcal mole ⁻¹	A^c sec ⁻¹	η^d cp
1 H ₂ O	6	10	8.5×10^{15}	0.89
2 D ₂ O	6	9	3.3×10^{19}	
3 CH ₃ OH	20	12.5	7.4×10^{16}	0.55
4 CH ₃ OD	21	11.7	1.8×10^{16}	
5 (CH ₂ OH) ₂	22			20*
6 (CH ₂ CH ₃) ₂ NH	22	9.7	5.9×10^{14}	0.35
7 CH ₃ COOH	26			1.16
8 glycerol	28			954
9 CH ₃ CH ₂ OH	29	10.0	7.4×10^{14}	1.1
10 <i>i</i> -propanol	31	10.0	6.9×10^{14}	1.8
11 THF	40	14.7	1.5×10^{18}	0.46
12 DMF	78			0.80
13 pyridine	87			0.97*
14 DMSO	89			2.2*
15 CH ₃ NO ₂	105			0.62
16 CH ₃ CN	106	11.4	2.2×10^{15}	0.35
17 CHCl ₃ ^e	106	11.1	1.3×10^{15}	0.54
18 CH ₃ COCH ₃	$139(2 \times 10^4)^h$	12.7	1.5×10^{16}	0.32
19 CH ₂ Cl ₂ ^f	175			0.39
20 <i>t</i> -butanol ^{e,f}	192	17.9	7.0×10^{19}	---
21 sulfolane ^f	204	14.0	9.1×10^{16}	---
22 solid ^g	406	5.6	2.8×10^{10}	---

(a) 530 nm stimulating pulse; emission detected at 750 nm. (b) 23°C.

(c) Frequency factor; see text. (d) 20°C if starred; otherwise 25°C.

(e) cryptate used to solubilize K⁺ ion. (f) Solid at 23°C; reported lifetime is that extrapolated to 23°C. (g) Powder suspended in CHCl₃. (h) At -87 to -20°C.⁵

Captions to Figures

- Figure 1. Energy level diagram for a Cr(III) complex. Q_0^0 is the ground state quartet, Q_{FC}^0 and Q_1^0 are the Franck-Condon and the hexi quartet states respectively. D_1^0 is the lowest doublet state.
- Figure 2. Emission spectrum of R^- in Acetonitrile at room temperature taken with optical multichannel analyzer: -----perdeuterated; ————undeuterated.
- Figure 3. Temperature dependence of emission from $\text{trans-Cr(NH}_3)_2(\text{NCS})_4^-$. Δ - Emission lifetime in Methanol; \circ - Emission lifetime in acetonitrile
- Figure 4. Barclay-Butler Plot of apparent activation energy, E^* , vs. frequency factor, A , from the equation: $1/\tau = A \exp(-E^*/RT)$. The numbers refer to the compounds in Table 1.
- Figure 5. Effects of water on R^- emission (left axis), Cr(CN)_6^{3-} emission (right axis), and photochemical NCS^- release (left internal axis; yields from reference 13) in acetonitrile-water mixtures. τ_0 is the lifetime in 100% acetonitrile and τ is the lifetime in the solvent mixtures. n/n_0 is the solvent sphere composition (fraction of water) around R^- in acetonitrile-water mixtures obtained from reference 13. MOLE FRACTION refers to the fraction of water in the bulk solvent. \circ - τ_0/τ R^- vs. Mole Fraction; \bullet - τ_0/τ R^- vs. n/n_0 ; \square - ϕ vs. Mole Fraction; $+$ - τ_0/τ Cr(CN)_6^{3-} vs. Mole Fraction.
- Figure 6. Doublet excited state absorption of R^- in acetonitrile at 20°C .

